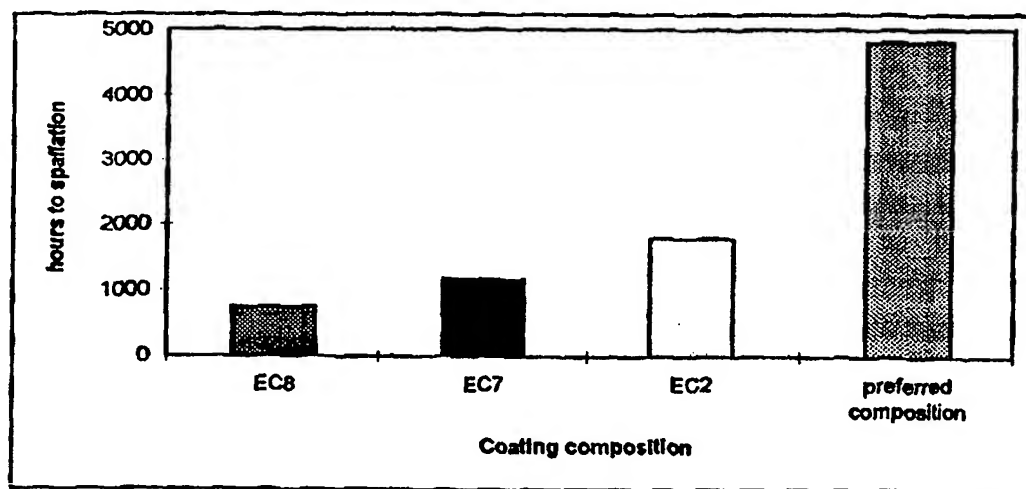




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(54) Title: HIGH TEMPERATURE PROTECTIVE COATING



(57) Abstract

The invention relates to a coating composition for superalloy structural parts, especially for gas turbine vanes and blades, comprising (in wt. %): Ni balance; Co 18-28; Cr 11-15; Al 11.5-14; Re 1-8; Si 1-2.5; Ta 0.2-1.5; Nb 0.2-1.5; Y 0.3-1.3; Mg 0-1.5; La + La series 0-0.5; B 0-0.1; Hf < 0.1; C < 0.1; where: Y + La (+ La-series) 0.3-2.0; Si + Ta < 2.5.

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High Temperature Protective Coating

Field of the Invention

The invention relates to an improved class of protective coatings for superalloy structural parts, especially for gas turbine vanes and blades.

Background of the Invention

In the field of gas turbine engines, designers continually look toward raising the operating temperature of the engine to increase efficiency. In turn, the oxidation rate of materials increases dramatically with increasing temperature. Gas turbine components can also be subjected to hot corrosion, when corrosive species are ingested into the engine via intake air and/or impurities in the fuel. Modern structural superalloys are designed for the ultimate in mechanical properties thereby sacrificing oxidation, and, to an even larger extent corrosion resistance.

To increase the useful life of gas turbine components it is customary to use protective coatings, such as aluminide or MCrAlY coatings where M may be Ni, Co, Fe or mixtures thereof. Since a coated turbine blade undergoes complicated stress states during operation, i.e. during heating and cooling cycles, advanced high temperature coatings must not only provide environmental protection but must also have specifically tailored physical and mechanical properties.

If the protective coating is to be used as a bond coat for thermal barrier coatings (TBCs) there are additional requirements. While for an overlay coating, i.e. no TBC, the thermally grown oxide can spall and regrow provided that the activity of Al in the coating remains sufficiently high, for a TBC bond coat oxide growth rate and oxide scale adherence are the life controlling parameters since if the oxide spalls, the TBC will spall. In summary, advanced high temperature protective coatings must meet the following requirements:

- high oxidation resistance,

- slowly growing oxide scale (low k_p value),
- good oxide scale adherence,
- hot corrosion resistance, superior to SX/DS superalloys,
- low interdiffusion of Al and Cr into the substrate to prevent the precipitation of brittle needle-like phases under the coating,
- creep resistance comparable to conventional superalloys
- high ductility at low temperatures and low ductile - brittle transition temperature
- thermal expansion coefficient similar to the substrate over the whole temperature range.

U.S. Pat. Nos. 5,273,712 and 5,154,885 disclose coatings with significant additions of Re which simultaneously improves creep and oxidation resistance at high temperatures. However, the combination of Re with high Cr levels, typical for traditional coatings, results in an undesirable phase structure of the coating and interdiffusion layer. At intermediate temperatures (below 950-900°C), α -Cr phase is more stable in the coating than the γ - matrix. This results in low toughness and low ductility. In addition, a significant excess of Cr in the coating compared to the substrate results in diffusion of Cr to the base alloy, which enhances precipitation of needle-like Cr-, W- and Re-rich phases.

U.S. Pat. No. 4,758,480 discloses a class of protective coatings whose compositions are based on the compositions of the underlying substrate. The similarities in microstructure (gamma prime phase in gamma matrix) render the mechanical properties of the coating similar to the mechanical properties of the substrate, thereby reducing thermomechanically induced damage during service. However, the contents of Al (7.5-11 wt%) and Cr (9-16 wt%) in the coating may not provide sufficient oxidation and/or corrosion resistance for the long exposure times which are customary in stationary gas turbines.

Object of the Invention

Accordingly, it is a main object of the invention to provide a new coating for structural parts of gas turbines, especially for blades and vanes, which exhibits improved me-

chanical behavior and which provides sufficient oxidation / corrosion resistance for the long exposure times which are customary in stationary gas turbines.

Summary of the Invention

The invention discloses a nickel base alloy, particularly adapted for use as coating for advanced gas turbine blading. The alloy is prepared with the elements in an amount to provide an alloy composition as shown in Table 1.

Table 1 Range of Coating Compositions of Present Invention

| Elements of composition (% by weight) | | | | | | | | | | | | |
|---|------|-------|-------|---------|-----|---------|-------|---------|---------|-------|-------|-------|
| | Ni | Co | Cr | Al | Re | Y | Si | Ta | Nb | La* | Mg | B |
| Coatin | bal. | 18-28 | 11-15 | 11.5-14 | 1-8 | 0.3-1.3 | 1-2.3 | 0.2-1.5 | 0.2-1.5 | 0-0.5 | 0-1.5 | 0-0.1 |
| La* = La + elements from Lanthanide series $Y + La (+ La\text{-series}) \leq 0.3-2.0$ $Si + Ta \leq 2.5 \text{ wt\%}$ $Hf, C < 0.1 \text{ wt\%}$ | | | | | | | | | | | | |

The alloy according to the invention provides simultaneously optimum oxidation and corrosion resistance, phase stability during diffusion heat treatment and during service, and mechanical behavior, especially high ductility, high creep resistance, and thermal expansion similar to the substrate.

This is achieved by a specific phase structure consisting of β -reservoir phase precipitates (45-60 vol%) in a ductile γ -matrix (40-55 vol%).

Preferably, the alloy can be produced by a vacuum melt process in which powder particles are formed by inert gas atomization. The powder can then be deposited on a substrate using, for example, thermal spray methods. However, other methods of application may also be used. Heat treatment of the coating using appropriate times and temperatures is recommended to achieve a good bond to the substrate and a high sintered density of the coating.

A number of different alloys with compositions according to the present invention, which have been tested, are given in Table 2 (a).

Table 2 (a) Preferred Coating Compositions

| Elements in wt% of composition | | | | | | | | | | | |
|--------------------------------|------|------|------|------|-----|-----|-----|-----|-----|-----|-----|
| | Ni | Co | Cr | Al | Re | Y | Si | Ta | Nb | La | Mg |
| PC1 | bal. | 24.1 | 11.8 | 12.1 | 2.8 | 0.3 | 1 | 1 | 0.3 | - | - |
| PC2 | bal. | 23.8 | 13 | 12 | 3 | 0.5 | 1.7 | 0.5 | 0.3 | - | 0.2 |
| PC3 | bal. | 23.8 | 13 | 11.8 | 3 | 0.3 | 1 | 1 | 0.3 | 0.1 | - |

These preferred alloys exhibit the desired coating behavior with optimum oxidation and corrosion resistance, phase stability during diffusion heat treatment and during service, and excellent mechanical behavior, especially high ductility, high creep resistance, and thermal expansion similar to the CMSX4 substrate material.

In order to prove the advantage of the preferred compositions a number of additional alloys whose compositions are given in Table 2 (b) have also been tested. Alloys EC1-EC8 were found to exhibit poor properties in comparison with the preferred compositions PC1, PC2, and PC3.

Table 2 (b) Additional Coating Compositions

| Elements in wt% of composition | | | | | | | | | | |
|--------------------------------|------|----|------|------|----|-----|-----|-----|-----|-----|
| Coating | Ni | Co | Cr | Al | Re | Y | Si | Ta | Nb | Hf |
| EC1 | bal. | 12 | 20.5 | 11.5 | - | 0.5 | 2.5 | 1 | - | - |
| EC2 | bal. | 12 | 16 | 11.5 | - | 0.3 | 2.5 | 1 | - | - |
| EC3 | bal. | 24 | 16 | 11 | - | 0.3 | 2 | 1 | - | - |
| EC4 | bal. | 24 | 13 | 11 | 3 | 0.3 | 2 | - | 0.5 | - |
| EC5 | bal. | 24 | 13 | 11.5 | 3 | 0.3 | 1.2 | - | - | 0.5 |
| EC6 | bal. | 24 | 14 | 11 | - | 0.3 | 2 | 0.5 | - | 0.5 |
| EC7 | bal. | - | 16 | 8 | - | 0.5 | 2 | 0.5 | - | - |
| EC8 | bal. | 12 | 8.5 | 7 | 3 | 0.5 | 1 | 3 | 0.3 | 0.7 |

Table 2 (c) Composition of CMSX4 (Single Crystal Base Material)

| Elements in wt% of composition | | | | | | | | | | |
|--------------------------------|------|----|-----|-----|-----|-----|-----|-----|----|-----|
| | Ni | Co | Cr | Al | Re | W | Mo | Ta | Ti | Hf |
| CMSX4 | bal. | 10 | 6.5 | 5.6 | 2.8 | 6.4 | 0.5 | 6.5 | 1 | 0.1 |

The beneficial phase structure of the preferred alloy compositions (β -phase in ductile γ matrix) is reflected by the results of tensile tests at RT and 400 °C (Table 3). While tensile specimens coated with EC1 fail below 0.4 % strain, specimens coated with the preferred compositions show tensile elongations of >4 % and >9 % at RT and 400 °C, respectively.

Table 3 Strain to Failure of selected coatings at RT and 400°C.

| coating | strain to failure at RT (%) | Strain to failure at 400 °C (%) |
|---------------|-----------------------------|---------------------------------|
| EC1 | <0.4 | <0.4 |
| EC2 | 0.8 | 1.9 |
| EC3 | 2 | 4.5 |
| EC4 | 2.2 | 4.8 |
| PC1, PC2, PC3 | >4 | >9 |

In addition, experimental TMF data (Table 4) show that the improved coatings of this invention also have superior TMF behavior. In contrast to coating EC1 which cracks at the first cycle and a conventional overlay coating which fails after 2000 cycles, the coatings according to the present invention have a TMF life of >3000 cycles, i.e. very similar to that of the uncoated single crystal base alloy.

Table 4 TMF life of selected coatings

| coating | No of cycles at failure |
|----------------------|-------------------------|
| EC1 | 1 |
| EC2 | <10 |
| conventional coating | 2000 |
| PC1, PC2, PC3 | >3000 |

The stable phase structure of the preferred compositions (45-60 vol% β and 55-40 vol% γ) is found to result in extremely high mechanical properties of coated specimens or components. This balance of two phases provides a unique combination of high TMF resistance and excellent oxidation resistance. Thermal expansion, ductility, and TMF resistance are on the level of the best $\gamma - \gamma'$ systems (such as single crystal superalloys), yet, the presence of the β reservoir phase results in an oxidation life which $\gamma - \gamma'$ systems cannot achieve.

It is important to understand that only the combination of the elements claimed in Table 1 results in the desirable $\beta + \gamma$ phase structure (in the requested phase proportions) with excellent oxidation/corrosion resistance and excellent mechanical properties. The excess of alloying elements, such as Cr, Al, Ta, Si, Nb, Co, Re, results in the precipitation of detrimental σ , Heusler-, or r-phases.

Lower than the specified levels of Al, Cr, Re, and Si lead to reduced oxidation and/or corrosion resistance. Reductions in the Ta and Nb content, or absence of at least one of said elements increases the rate of oxide growth, and hence, should be avoided in case that the coating is to be used as a TBC bond coat.

Changing the balance between Al, Cr, and Co may result in a similar initial phase structure but this phase structure is not expected to be stable during service. Phase transformations have been shown to result in increased thermal expansion mismatch between coating and substrate (as shown) and therefore reduced service life.

Although this invention has been shown and described with respect to a preferred embodiment, it will be understood by those skilled in this art that various changes in form and detail thereof may be made without departing from the spirit and scope of the claimed invention.

Brief Description of the Drawings

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

- Fig. 1 shows the function of the Al activity vs. Cr content in the alloy (other elements as follows: 12.1% Al, 24.1% Co, 3% Re, 1% Si, 0.5% Ta);
- Fig. 2 shows the function of the Al activity vs. Re content in the alloy (other elements as follows: 12.1% Al, 11.8% Cr, 24.1% Co, 1% Si, 0.5% Ta);
- Fig. 3 shows the function of the Al activity vs. Si content in the alloy (other elements as follows: 12.1% Al, 11.8% Cr, 24.1% Co, 3% Re, 0.5% Ta);
- Fig. 4 shows the function of the mass increase per unit area vs. oxidation time as a result of oxidation at 1000 °C for the preferred coating compositions PC1, PC2, PC3 and of experimental coatings EC3, EC4, EC5, EC6, and EC8;
- Fig. 5 shows the function of the spallation time for first oxide scale spallation at 1050 °C vs. coating composition in the form of a bar chart,
- Fig. 6 (a) shows in a diagram the function of the X-ray intensity vs. oxidation time by in situ X-ray analysis during oxidation at 1000 °C for the preferred compositions PC1, PC2, PC3.
- Fig. 6 (b) shows a second chart of the function of the X-ray intensity vs. oxidation time by in situ X-ray analysis during oxidation at 1000 °C for the case when transient oxide formation takes place.
- Fig. 7 (a) shows a first chart of the equilibrium phase structures for the preferred coating composition.
- Fig. 7 (b) shows a second chart of the equilibrium phase structures for experimental coating composition EC7.
- Fig. 8 shows a chart of the function of the coefficients of thermal expansion of CMSX4, experimental coating EC7, and the alloy composition of the present invention vs. temperature.

Detailed Description of the Charts

The oxidation resistance of the alloy has been found to be determined mainly by its Al content, i.e. by the reservoir of Al atoms to form a protective Al_2O_3 scale, and by the activity of Al in the system. The activity of Al is strongly influenced by the presence of other elements in the alloy and by the alloy phase structure which determines Al-diffusion. Modeling results on the influence of Cr, Re and Si on Al activity, and hence, oxidation resistance of the alloy are presented in Figs. 1-3.

Upon oxidation the alloy shows an increase in weight due to the uptake of oxygen. If the growing oxide scale is protective the weight gain as a function of oxidation time follows a parabolic rate law. Obviously, a small weight increase is indicative of a slowly growing oxide scale and, thus, is a desirable property.

Presented in Fig. 4 are experimental data which show that the weight change is lowest for the preferred alloy compositions when compared to experimental alloys EC3, EC4, EC5, EC6, and EC8. The poor oxidation behavior of EC8 illustrates the necessity of having a sufficiently high content of Al and of other elements supporting the Al activity in the alloy.

Apparently, certain elements in the preferred composition act by modifying the oxide layer so as to render it more resistant to the inward diffusion of oxygen or the outward diffusion of Al. Oxide growth continues until a critical oxide thickness is reached and spallation occurs. As long as Al content and Al activity in the alloy remain sufficiently high the Al_2O_3 scale can grow and spall repeatedly.

Typically, MCrAlY coatings contain 0.5 to 1 wt% Y which has a powerful effect on the oxidation resistance of the alloy. In some fashion, Y acts to improve the adherence of the oxide scale which forms on the coating, thereby substantially reducing spallation. A variety of other so-called oxygen active elements (La, Ce, Zr, Hf, Si) have been proposed to replace or supplement the Y content.

In the present invention Y is added in amounts on the order of 0.3 to 1.3 wt%, La and elements from the Lanthanide series in amounts ranging from 0 to 0.5 wt%. Surprisingly, Hf was found here to increase the rate of oxide growth. The difference in oxidation rate for the preferred alloy compositions (i.e. Hf-free) and Hf-containing alloys (EC5, EC6, and EC8) is demonstrated in Fig. 4. Energy dispersive X-ray analysis revealed the presence of Hf carbides in Hf-containing alloys which are likely to reduce oxidation resistance.

Nb and Ta, on the other hand, were found to increase oxidation resistance by reducing the rate of oxide growth. Their cumulative effect is stronger than the influence of any one of them taken separately. In the presence of Ta even small amounts of Nb on the order of 0.2 to 0.5 wt% can have a significant effect on oxidation resistance (compare the preferred composition with EC3 and EC4 in Fig. 4).

The corrosion resistance of the alloy is determined mainly by the Cr content in the alloy. When tested in a corrosive environment ($\text{NaSO}_4/\text{CaSO}_4$ slag + air/ SO_2 atmosphere) for 2000 hr the various alloy compositions show depths of corrosion attack ranging from a few μm to mm. While CMSX4 (6.5 wt% Cr) is totally corroded, the preferred alloy compositions PC1, PC2, PC3 (11-15 wt% Cr) show signs of attack only within a 5 μm zone. Low Cr levels (< 11%) result not only in low corrosion resistance, but also in a lower Al activity and hence, lower oxidation resistance. It is obvious from Fig. 1 that the Al activity increases significantly if the Cr level is >11%. Too high a Cr level, particularly in combination with a high Al content, however, significantly reduces low temperature ductility and fatigue life. At Cr levels exceeding 16 wt%, β and γ phases transform to α -Cr and γ' during service operation, resulting in a totally brittle phase structure.

Co increases the solubility of Al in the γ matrix, and as a consequence, suppresses the amount of brittle phases (particularly σ) present in the alloy. Comparing the RT ductility of specimens coated with EC2 and EC3 (Table 3) clearly demonstrates the beneficial role of Co.

The presence of Si in the alloy increases the activity of Al (Fig. 3) and, thus, its oxidation resistance. Si contents > 2.5 wt%, however, must be avoided in order to prevent precipitation of brittle Ni (Ta, Si) phases. The beneficial role of Ta on oxidation performance, particularly when combined with Si, is already known from EP Pat. No. 0 241 807. However, computer modeling of the phase structure shows that in order to avoid embrittlement of the coating the combined content of (Si + Ta) must not exceed 2.5 wt%.

Commercial structural superalloys are strengthened not only by gamma prime forming elements (Al, Ti, Ta) but by additions of solid solution strengtheners such as Re, W, Mo, Cr, Co. Since W and Mo have been found to be detrimental to oxidation resistance they can be replaced by Re and Ta without loss in strength. From Fig. 2 it is clear that Re increases the activity of Al in the alloy, and, hence has a positive effect

on oxidation performance. Re is also known to improve microstructural stability and reduce interdiffusion.

The improved coatings of this invention are also useful as bond coats for thermal barrier coatings (TBC). A typical TBC system is a two-layer material system consisting of a ceramic insulator (e.g. Y_2O_3 partially stabilized ZrO_2) over an MCrAlY bond coat. Since TBC life significantly depends on the amount of oxide grown at the bond coat / ceramic interface oxide growth rate and oxide scale adherence are among the life controlling parameters.

While for an overlay coating (i.e. no TBC) the thermally grown oxide can spall and regrow repeatedly, for a TBC system oxide spallation during service is to be strictly avoided. Oxidation experiments were carried out on different coating compositions and the oxidation time (in hrs) required until first spallation occurs was determined.

These data have been plotted in Fig. 5, where it can be seen that the time to first spallation which is indicative of the oxide scale adherence is longest for the preferred coating compositions PC1, PC2, PC3.

Of great importance for a TBC bond coat is also the formation of a protective $\alpha-Al_2O_3$ scale during the initial phase of oxidation. Transient oxides which have higher growth rates than Al_2O_3 add to the amount of oxide but not to its protective nature.

Hence, the presence of transient oxides at the bond coat / ceramic interface must be avoided or kept at a minimum. Different approaches, such as diffusion of Al or Pt, into the outer portion of the bond coat have been proposed to promote the formation of $\alpha-Al_2O_3$. Diffusion enriched layers, however, typically suffer from inferior mechanical properties due to the precipitation of brittle phases.

In situ X-ray analysis performed during oxidation of different alloys at 1000 °C revealed the following: a protective $\alpha-Al_2O_3$ scale had formed on the preferred compositions PC1, PC2, PC3 within 1 hr of oxidation, transient oxides could not be detected (even at glancing angle). In addition to $\alpha-Al_2O_3$, only $AlYO_3$ which grows close to the Al_2O_3 / substrate interface and promotes the mechanical interlocking of the oxide scale appears in the X-ray spectrum. Fig. 6 (a) shows the results of in situ X-ray analysis of the preferred composition, while Fig. 6 (b) illustrates the case when transient oxide formation takes place.

Fig. 7 (a) shows the phases present in the preferred coating compositions as a result of computer modeling. The phase structure which consists of 45-60 vol% beta and 55-40 vol% gamma is seen to be stable over a wide temperature range (approx. 900-1280 °C). Upon cooling only a small alloy volume (< 10 vol%) will undergo a detrimental phase transformation $\beta + \gamma \rightarrow \sigma + \gamma'$. This large region of phase stability makes the coatings rather insensitive to diffusion heat treatment temperatures. In contrast, computer modeling of experimental coating EC7 (Fig. 7 (b)) yields a stable phase composition only at temperatures below 980°C and massive phase transformations involving a large alloy volume above 980 °C.

Phase transformations in the alloy during heating/cooling cycles have a pronounced effect on the physical properties and, as a consequence, on the mechanical behavior of the alloy. This is illustrated in Fig. 8 where the coefficients of thermal expansion are shown for CMSX4 (base alloy), the preferred alloy compositions and alloy EC7. While the preferred compositions and CMSX4 show nearly linear behavior over the whole T range, the deviation from linearity for EC7 coincides with the onset of phase transformations at T~950 °C. It is understood that large differences in thermal expansion between coating and substrate lead to high total mechanical strains in the coating.

Claims

1. A coating composition for superalloy structural parts, especially gas turbine vanes and blades, comprising (in % by weight):

| | | | |
|----|-----------|-----------------------------|-----------|
| Ni | balance | Y | 0.3 - 1.3 |
| Co | 18 - 28 | Mg | 0 - 1.5 |
| Cr | 11 - 15 | La + La-series | 0 - 0.5 |
| Al | 11.5 - 14 | B | 0 - 0.1 |
| Re | 1 - 8 | Hf | < 0.1 |
| Si | 1 - 2.3 | C | < 0.1 |
| Ta | 0.2 - 1.5 | where: Y + La (+ La-series) | 0.3-2.0 |
| Nb | 0.2 - 1.5 | Si + Ta | ≤ 2.5 |

2. The coating composition of claim 1 comprising

| | | | |
|----|---------|---------|-------|
| Ni | balance | Si | 1 |
| Co | 24.1 | Y | 0.3 |
| Cr | 11.8 | Ta | 1 |
| Al | 12.1 | Nb | 0.3 |
| Re | 2.8 | Si + Ta | ≤ 2.5 |

3. The coating composition of claim 1 comprising

| | | | |
|----|---------|---------|-------|
| Ni | balance | Y | 0.5 |
| Co | 23.8 | Ta | 0.5 |
| Cr | 13 | Nb | 0.3 |
| Al | 12 | Mg | 0.2 |
| Re | 3 | Si + Ta | ≤ 2.5 |
| Si | 1.7 | | |

4. The coating composition of claim 1 comprising

| | | | |
|----|---------|---------|------------|
| Ni | balance | Y | 0.3 |
| Co | 23.8 | Ta | 1 |
| Cr | 13 | Nb | 0.3 |
| Al | 11.8 | La | 0.1 |
| Re | 3 | Si + Ta | ≤ 2.5 |
| Si | 1 | | |

5. The coating composition of claim 1 comprising a phase structure of ductile γ matrix containing β precipitates being beneficial for oxidation/corrosion resistance and mechanical behavior.

6. The coating composition according to claim 1 being deposited as a layer on a substrate selected from the group consisting of Ni-base and Co-base superalloys.

7. The coating composition according to at least one of the preceeding claims being deposited as a layer on a substrate and provided with a top layer of a thermal barrier coating of said coating composition.

8. Powder composition according to one of the preceeding claims 1 to 4 provided as source material for the coating according to one of the claims 5 to 7.

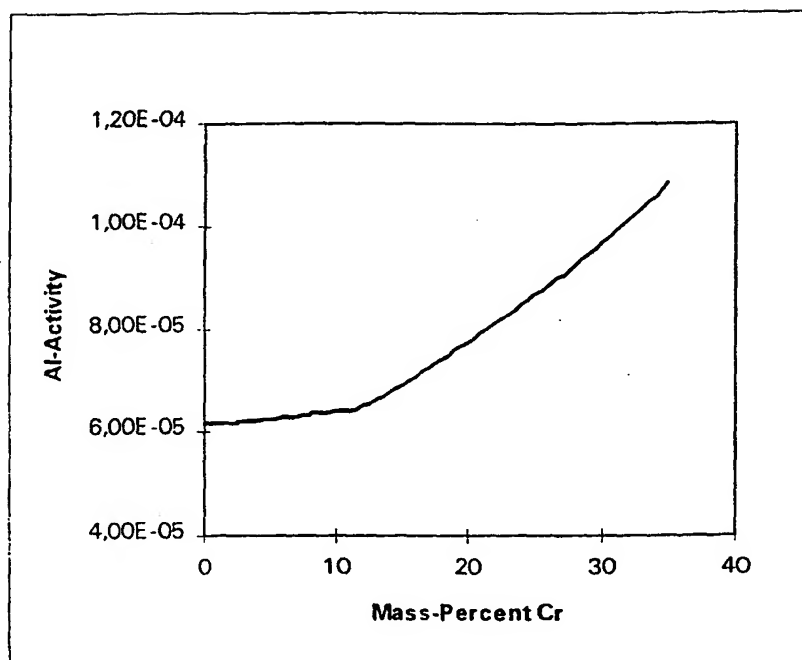


Fig. 1

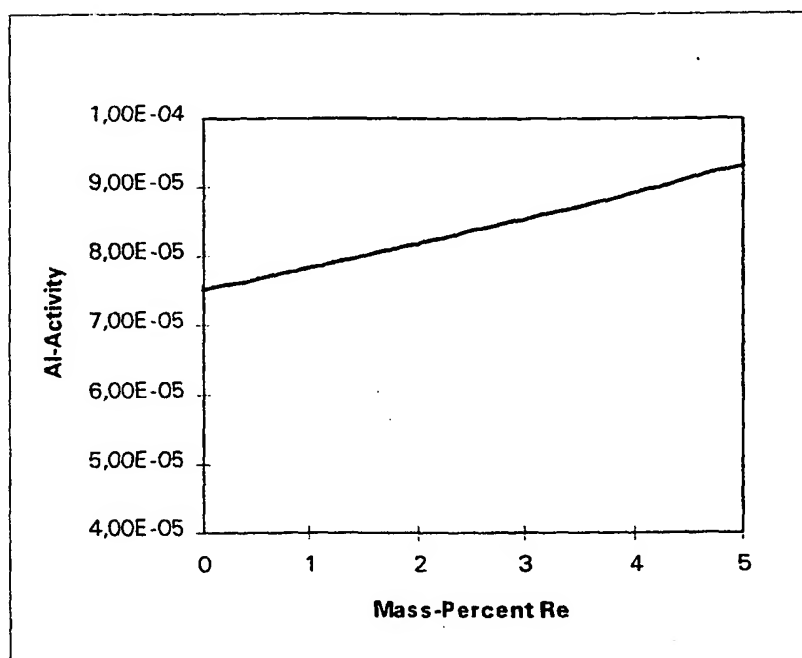


Fig. 2

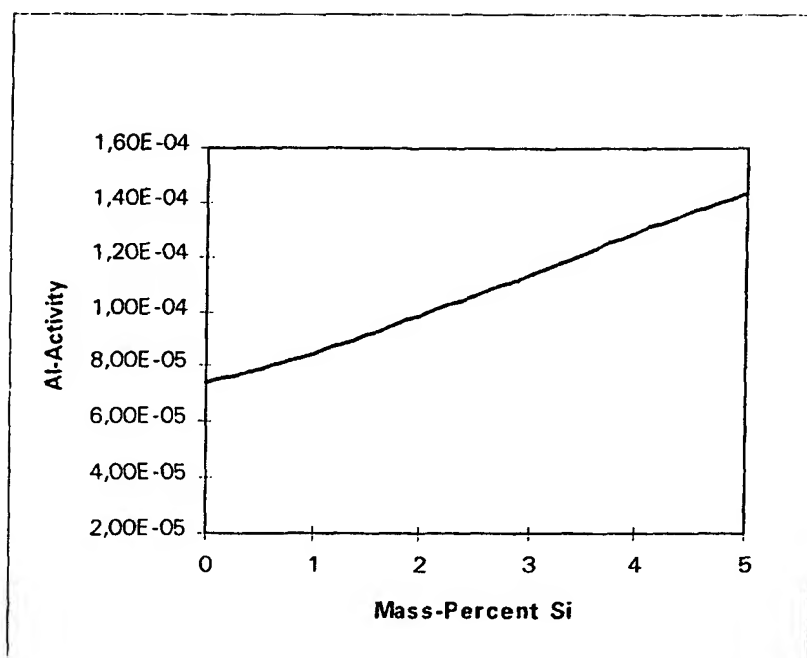


Fig. 3

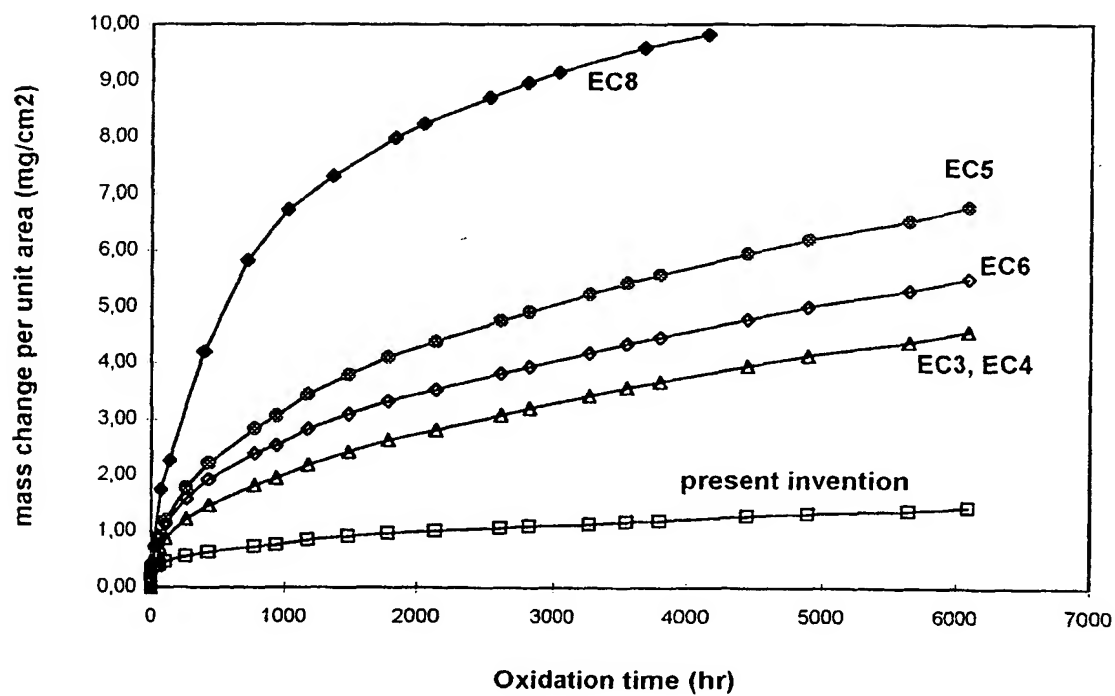


Fig. 4

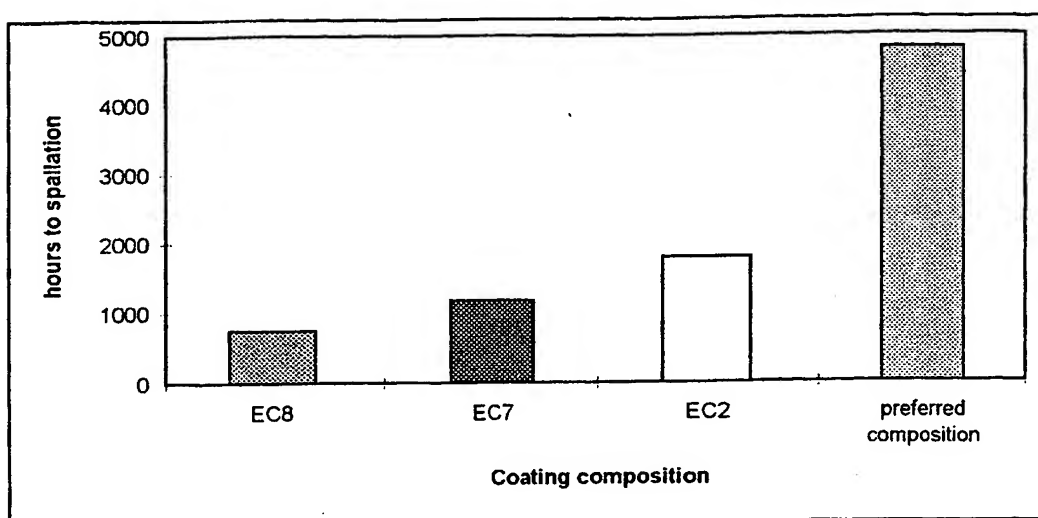


Fig. 5

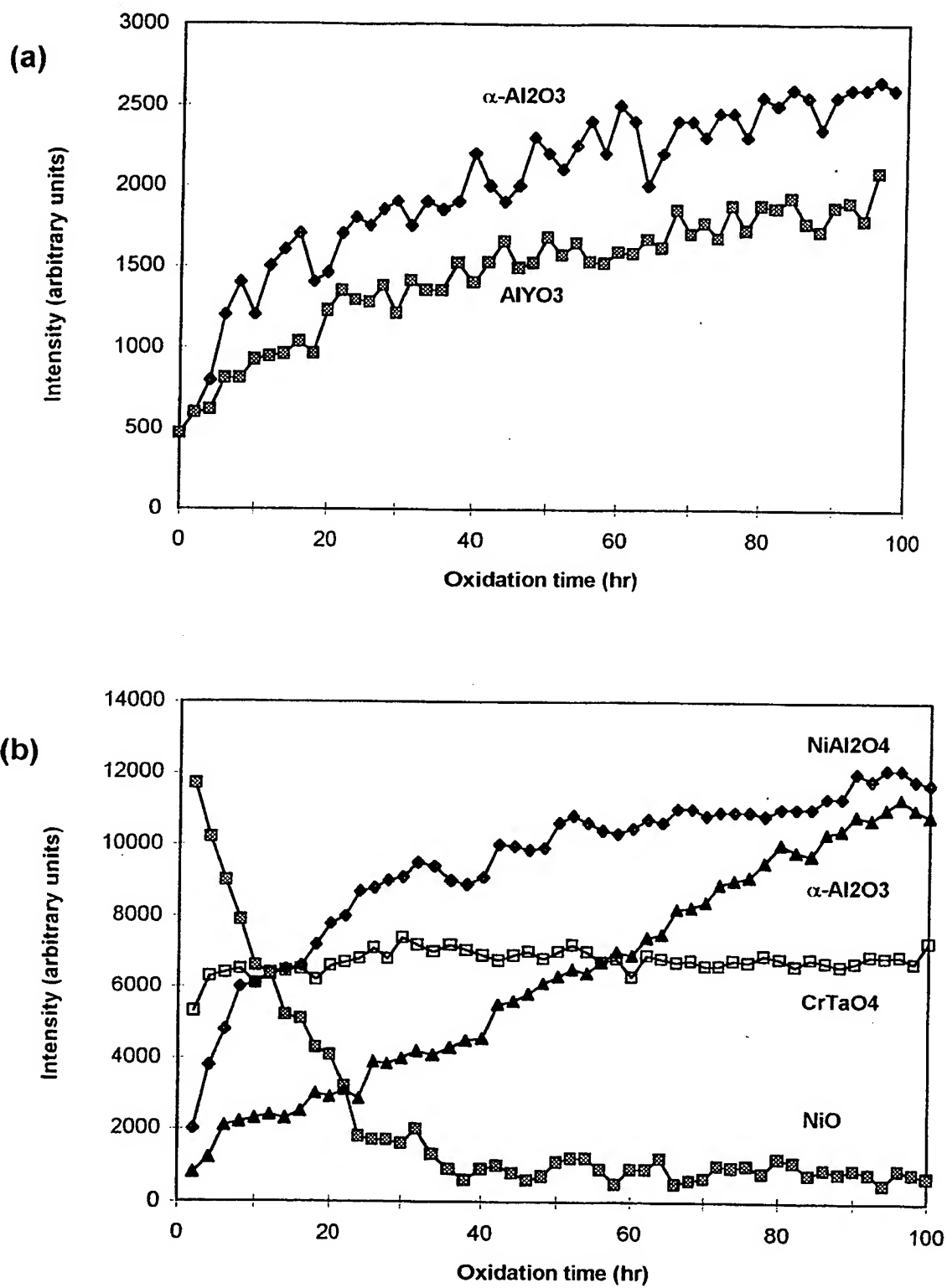


Fig. 6

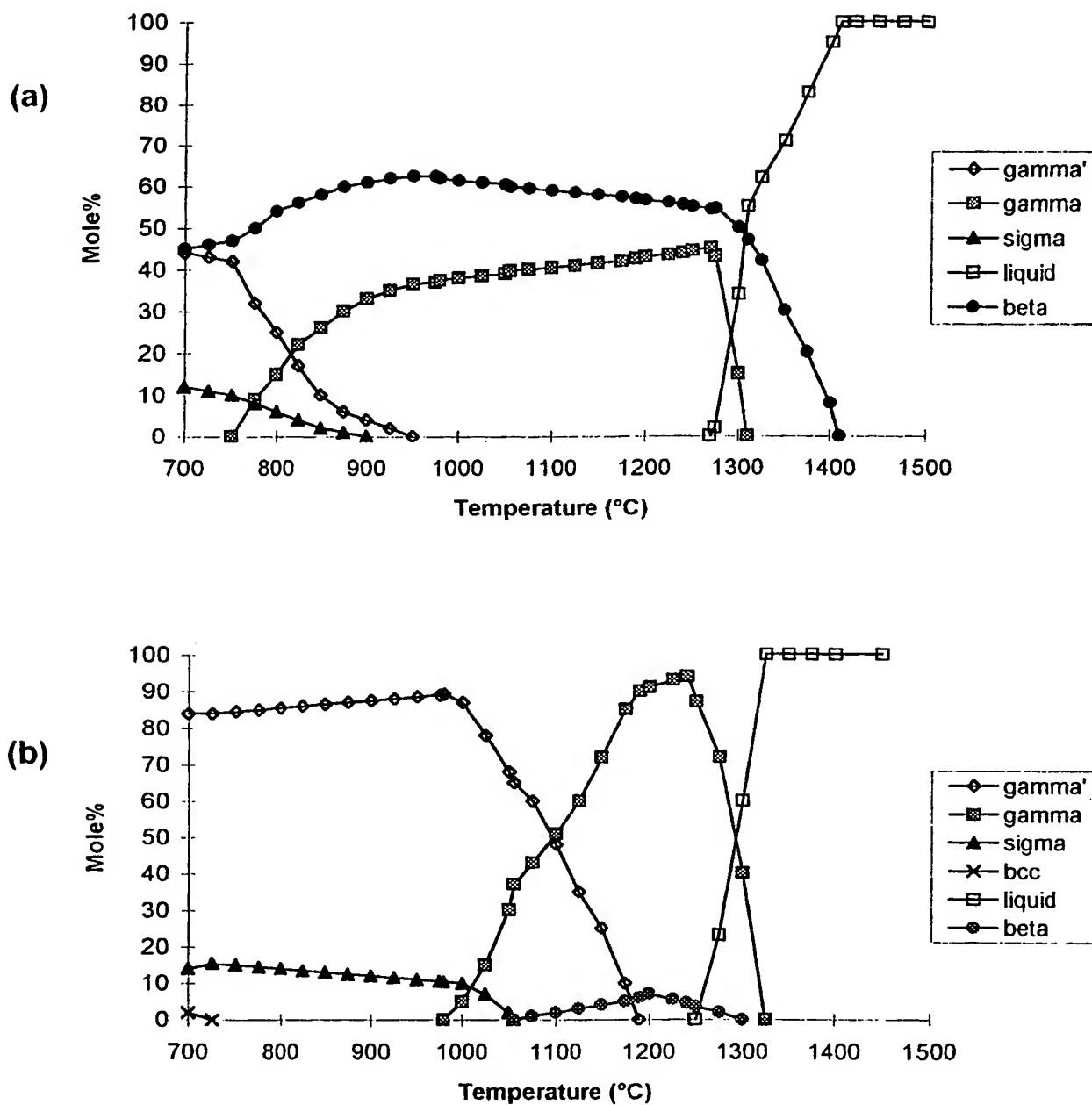


Fig. 7

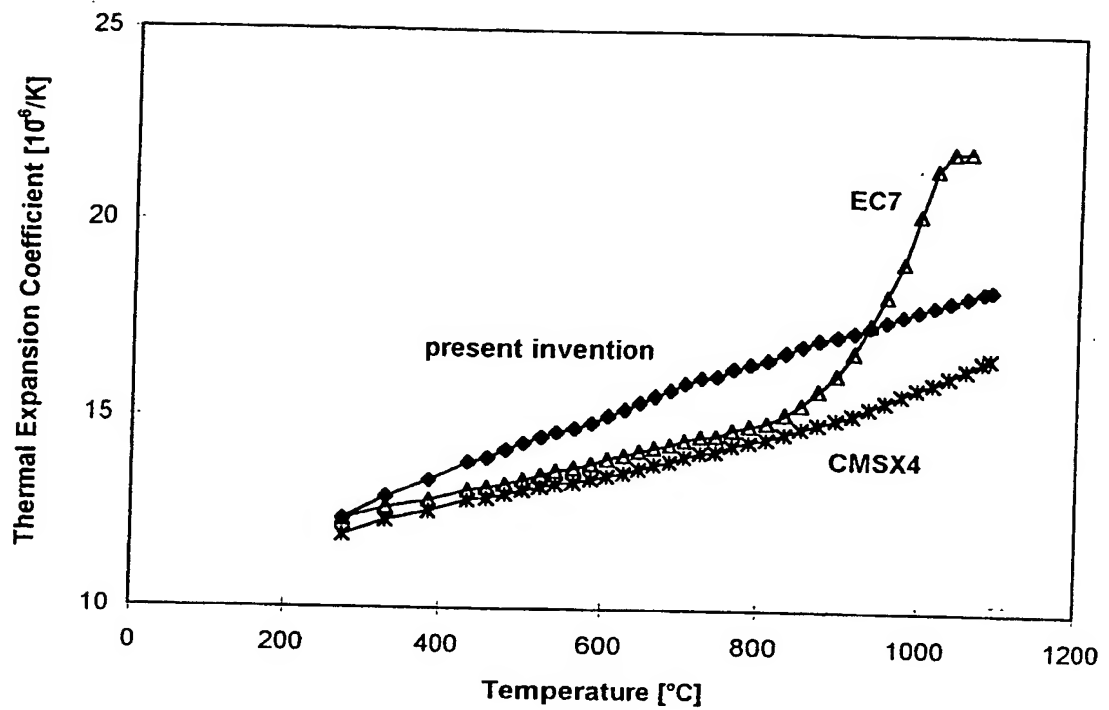


Fig. 8

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/06000

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C30/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | US 5 273 712 A (CZECH NORBERT ET AL) 28 December 1993 cited in the application see claims 1-9 --- | 1 |
| A | WO 96 12049 A (SIEMENS AG ; SCHMITZ FRIEDHELM (DE); CZECH NORBERT (DE)) 25 April 1996 see claim 1 --- | 1 |
| A | DE 94 15 168 U (SIEMENS AG) 17 November 1994 see claim 1 ----- | 1 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

26 May 1998

Date of mailing of the international search report

04/06/1998

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Authorized officer

Gregg, N

INTERNATIONAL SEARCH REPORT

Information on patent family members

I. International Application No

PCT/EP 97/06000

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| | | US 5268238 A | 07-12-1993 |
| | | DE 59010817 D | 30-04-1998 |
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| | | JP 3120327 A | 22-05-1991 |
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| DE 9415168 U | 17-11-1994 | NONE | |

